Selective Excitation Switching Angle Sample Spinning 13C NMR Study of the Local Motion of Glassy Polymers (FUNDAMENTAL MATERIAL PROPERTIES - Molecular Motion Analysis)

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Natural abundant ^{13}C chemical shift anisotropy (CSA) spectra of the aromatic CH carbons of bisphenol-A (BPA) residues have been measured for BPA polycarbonate (BPAPC) and polyarylate (PAr) films at different temperatures by the selective excitation switching angle sample spinning (SESASS) NMR spectroscopy. The CSA spectra thus obtained have been analyzed in terms of the two-site exchange model for the flip motion of the phenylene group. In BPAPC and PAr, wide distributions in flip angle around 0° and 180° are well revealed under the situation of the first exchange limit for the flip motion and the widths become significantly broader with increasing temperature. Moreover, the onset of the additional larger-scale motion of the flip axis is suggested above 60°C for PAr.

Keywords: High-Resolution Solid-State ^{13}C NMR/ Chemical Shift Anisotropy/ Two-Site Exchange Model/ Glassy Polymers/ Polycarbonates/ Molecular Motion

High-resolution solid-state ^{13}C NMR spectroscopy is a very powerful tool for characterizing molecular dynamics of glassy polymers. In particular, since the natural abundant ^{13}C nuclei are used in this method, the molecular motions of the respective carbons constituting polymer chains are well analyzed without using any labelling technique. As for the mid-kHz motion, lineshpe analyses of ^{13}C chemical shift anisotropy (CSA) spectra seem to be one of the most suitable ways for glassy polymers. Although many sophisticated methods have been proposed for the measurements of CSA spectra, selective excitation switching angle sample spinning (SESASS) is a very convenient and timesaving method to measure CSA spectra because this is one-dimensional spectroscopy involving the cross polarization (CP), DANTE pulse sequence and SASS.

This report deals with measurements of the CSA spectra of the phenylene carbons of bisphenol-A residues for polycarbonate (BPAPC) or polyarylate (PAr) films at different temperatures by SESASS and analyses of those spectra in terms of the two-site exchange model considering the flip motion of the phenylene group.

BPAPC pellets, which were provided by Teijin Chemicals, Ltd., were hot-pressed at 320°C under 150 kg/cm^2 and quenched in iced water. PAr which is a noncrystalline polymer composed of BPA and phthalic acid (50% terephthalic acid + 50% isophthalic acid) residues, was provided as films by Unitika Ltd. ^{13}C NMR measurements were conducted on a JEOL JNM-GSX200 spectrometer operating under a static magnetic field of 4.7 T. ^{13}C CSA spectra were obtained with the use of a Doty Scientific DAS probe.

FUNDAMENTAL MATERIAL PROPERTIES —Molecular Motion Analysis—

Scope of research

The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, and solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.

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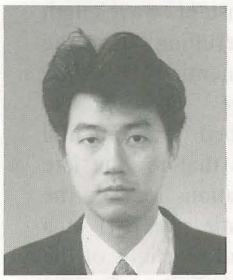

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Figure 1(a) shows 50 MHz CP/MAS ^{13}C NMR spectrum of BPAPC measured at 25°C . Almost no spinning side band appears for the C5 carbon as well as other aromatic and carbonyl carbons at the spinning with 7 kHz. First we have examined the selective observation of the C5 carbon by using the DANTE pulse sequence under the MAS condition. The result is shown in Figure 1(b). Since only the C5 resonance line can be observed, the selective excitation seems to be satisfactorily carried out for the C5 line by DANTE.

Figure 1(c) shows the CSA spectrum of the C5 carbon which was measured by the exact SESASS pulse sequence. The spinning angle $\theta_s=45°$ seems to be suitable for the detection of the CSA with the enough precision. The CSA spectrum thus obtained is scaled along the frequency axis by setting the isotropic resonance center as an origin. In such a case the scaling factor f_s is expressed as $(3\cos^2\theta_s-1)/2$. Considering this factor, the descaled spectrum (Figure 1(d)) has been obtained simply by using the scaling factor $f_s=0.25$. The CSA line shape thus obtained seems to be almost axially symmetric, suggesting the enhanced flip motion of the phenylene group even at room temperature.

The descaled CSA spectra obtained at different temperatures for the C5 carbon were compared with computer-simulated spectra which were obtained by using the two-site exchange model for the phenylene motion. In this case the phenylene group is assumed to undergo the flip motion with a flip angle δ between two sites.

Any simple flip motion including the 180° flip motion is not successful to reproduce the experimental CSA spectra. Therefore, we have introduced wide distributions of the flip angle δ around 0° and 180° assuming Gaussian distribution curves. Here, two distributions in δ indicate two types of flip motions which are allowed between 0° and an angle less than 90° and between 0° and another δ that is described by $90°<\delta<180°$. The simulated spectra are in good accord with the observed spectra at the respective temperatures except for the upfield small deviation at higher temperatures. According to this analysis, the flip frequency κ is found to be in the fast exchange limit ($\kappa>10^5$ Hz), which must be favorable for the detection of the distribution in flip angle. Moreover, the distribution width is increased with increasing temperature and the occurrence of the flip around 180° is also enhanced compared to the case around 0°. The upfield disagreement between the observed and simulated spectra at higher temperatures may suggest the onset of the thermal fluctuation of the flip axis of the phenylene ring.

To estimate the order of the flip frequency of the phenylene motion, the temperature dependency of ^{13}C

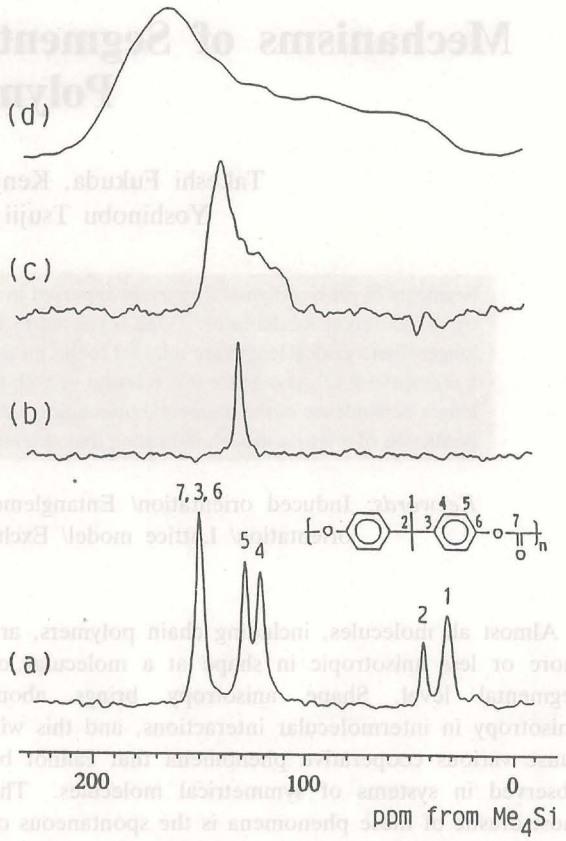

Figure 1. Solid ^{13}C NMR spectra of BPAPC. As for the explanation of each figure, see text.

spin-lattice relaxation times for the C5 carbon of BPAPC has been analyzed by the model-free treatment previously proposed. The simulated results considering two kinds of random motions with different correlation times are in good accord with the observed data. It is, therefore, concluded that the slower motion should be assigned to the flip motion around 180° for the phenylene group, which has the correlation time of about 10^8 Hz at room temperature. On the other hand, the correlation time for the faster motion assigned to the rapid fluctuation around the potential minimum is found to be of the order of 10^{12} Hz.

Similar SESASS measurements have been applied for the aromatic CH carbon of PAr at −30–100°C. The CSA spectra obtained at lower temperatures can be also well analyzed in terms of the two-site exchange model as the case of BPAPC and wider distributions in flip angles are found to exist in PAr compared to the case of BPAPC. Moreover, the phenylene flip axis may undergo additional larger-scale fluctuation above 60°C in this polymer. Further investigations are in progress to characterize the detailed motions even at temperatures near the glass transition temperatures.